



AU9176989

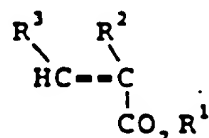
(12) PATENT ABRIDGMENT (11) Document No. AU-B-76989/91  
(19) AUSTRALIAN PATENT OFFICE (10) Acceptance No. 651102

- (54) Title  
MILDNESS ADDITIVES FOR SKIN CLEANSING COMPOSITIONS
- (51)<sup>5</sup> International Patent Classification(s)  
A61K 007/48 A61K 007/50 C11D 003/37 C11D 009/28
- (21) Application No. : 76989/91 (22) Application Date : 09.04.91
- (87) PCT Publication Number : WO91/16037
- (30) Priority Data
- (31) Number (32) Date (33) Country  
509461 16.04.90 US UNITED STATES OF AMERICA
- (43) Publication Date : 11.11.91
- (44) Publication Date of Accepted Application : 14.07.94
- (71) Applicant(s)  
MINNESOTA MINING AND MANUFACTURING COMPANY
- (72) Inventor(s)  
NEIL A RANDEN; ROBERT W.H. CHANG
- (74) Attorney or Agent  
SPRUSON & FERGUSON, GPO Box 3898, SYDNEY NSW 2001
- (56) Prior Art Documents  
US 4552755
- (57) Claim

1. A skin-cleansing composition consisting essentially of

a) a cleansing component selected from a soap composition, a soap/synthetic "combo" composition or a synthetic detergent composition, said cleansing component characterized by having the effect of drying or irritating skin, and

b) a non-water soluble acrylate polymer that is soluble in poorly hydrogen bonding solvents or solvent blends that have a solubility parameter of between about 8.4 and 10.4 (cal/cc)<sup>1/2</sup> in an amount effective to reduce the drying or irritating effect of component a) on the skin, said polymer comprising monomers of the formula:



wherein R<sup>1</sup> is H or an alkyl radical containing 1 to 18

(11) AU-B-76989/91  
(10) 651102

-2-

carbon atoms in cyclic, straight- or branched-chain configuration and is saturated or unsaturated;  $R^2$  is hydrogen, lower alkyl or  $-CH^2CO_2R^1$ ; and  $R^3$  is hydrogen, methyl or  $--CO_2R^1$ ; provided, that when  $R^2$  is not hydrogen,  $R^3$  is hydrogen, and when  $R^3$  is not hydrogen,  $R^2$  is hydrogen.

PCT AOJP DATE 19/12/91

PCT NUMBER PCT/US91/02443

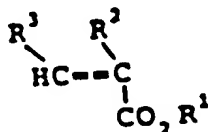
INTERNATIONAL

(PCT)

(51) International Patent Classification <sup>5</sup> : A61K 7/48, C11D 3/37		A1	(11) International Publication Number: WO 91/16037
			(43) International Publication Date: 31 Oct ber 1991 (31.10.91)
(21) International Application Number: PCT/US91/02443 (22) International Filing Date: 9 April 1991 (09.04.91) (30) Priority data: 509,461 16 April 1990 (16.04.90) US (60) Parent Application or Grant (63) Related by Continuation US 509,461 (CIP) Filed on 16 April 1990 (16.04.90) (71) Applicant (for all designated States except US): MINNESOTA MINING AND MANUFACTURING COMPANY [US/US]; 3M Center, Post Office Box 33427, Saint Paul, MN 55133-3427 (US).		(72) Inventors; and (75) Inventors/Applicants (for US only) : RANDEN, Neil, A. [US/US]; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). CHANG, Robert, W., H. [US/US]; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (74) Agent: BJORKMAN, Dale, A.; Post Office Box 33427, Saint Paul, MN 55133-3427 (US). (81) Designated States: AT (European patent), AU, BE (European patent), BR, CA, CH (European patent), DE (European patent), DK (European patent), ES (European patent), FR (European patent), GB (European patent), GR (European patent), IT (European patent), JP, LU (European patent), NL (European patent), SE (European patent), US. Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.	

651102

(54) Title: MILDNESS ADDITIVES FOR SKIN CLEANSING COMPOSITIONS



(I)

## (57) Abstract

Skin-cleansing compositions with a mildness additive that is a non-water soluble acrylate polymer that is soluble in poorly hydrogen bonding solvents or solvent blends having a solubility parameter of between about 8.4 and 10.4 (cal/cc)<sup>1/2</sup>. The polymer comprises monomers of formula (I), wherein R<sup>1</sup> is H or an alkyl radical containing 1 to 18 carbon atoms in cyclic, straight- or branched-chain configuration and is saturated or unsaturated; R<sup>2</sup> is hydrogen, lower alkyl or -CH<sub>2</sub>CO<sub>2</sub>R<sup>1</sup>; and R<sup>3</sup> is hydrogen, methyl or -CO<sub>2</sub>R<sup>1</sup>; provided, that when R<sup>2</sup> is not hydrogen, R<sup>3</sup> is hydrogen, and when R<sup>3</sup> is not hydrogen, R<sup>2</sup> is hydrogen. The incorporation of the indicated polymers reduces the drying and irritating effect of conventional cleansing compositions on the skin.

## MILDNESS ADDITIVES FOR SKIN CLEANSING COMPOSITIONS

### Technical Field

5       The invention relates to mildness additives for skin cleansing compositions. More specifically, it relates to polymeric mildness additives for skin cleansing bars and liquids.

### 10       Background of the Invention

      Since early time, people have combined fats and p tash to create compositions that would be useful as a cleanser, especially for the skin. Over the years variations and  
15       improvements have been made to provide a wide selection of cleansing products with different properties.

      U.S. Patent No. 2,820,768 to Fromont discloses transparent toilet soaps in a solid form consisting of (1)  
20       a transparent sodium soap prepared by saponification of a mixture of tallow, coconut oil and castor oil, (2) a triethanolammonium salt of stearic acid, and (3) a quantity of triethanolamine in excess over the theoretical amount required to fully neutralize the fatty acid and amounting  
25       to no less than one mole and no more than two moles per mole of soap forming fatty acid. The toilet bar is described as being both transparent and hard.

      U.S. Patent No. 3,406,238 to Freyermuth et al. discloses toiletry and cosmetic compositions comprising as  
30       an essential component from 0.1 to about 50% by weight of an alkylated polymer of an N-vinyl heterocyclic monomer. At least 25% on average of the N-vinyl heterocyclic monomer units in the polymer are alkylated with an alkyl group of from 10 to 42 carbon atoms. The presence of this additive  
35       in these preparations is disclosed to impart a much smoother texture to the composition and a softening and soothing effect of the composition when applied to the skin.

U.S. Patent No. 3,503,888 to Miller et al. discloses a synthetic detergent toilet bar in which an anionic type detergent is a major component and which has a soapy or slippery feel, good sudsing and rinsability characteristics, and leaves the skin feeling soft and smooth with no tacky sensation. The synthetic detergent toilet bar thus disclosed contains three essential components: a fatty acid ester of a sulfonated phenol, a salt of the fatty acid, and a salt of the sulfonated phenol.

U.S. Patent No. 4,673,525 to Small et al. discloses mild skin cleansers comprising synthetic surfactants, moisturizers, polymeric "skin feel" and mildness aids and soap. The polymeric "skin feel" and mildness aids are fully discussed at col. 7, line 43 to col. 8, line 49. These aids are disclosed to be the cationic, anionic, amphoteric, and the nonionic polymers used in the cosmetic field. The nonionic polymers to be used are disclosed at col. 8, line 11-18, as nonionic polysaccharides and cellulosic nonionic polymers. The disclosure of cationic polymers allows that these polymers may be copolymers with dimethylaminoethylmethacrylate and acrylamide and copolymers of dimethyldiallylammonium chloride and acrylamide, but specifically requires that the ratio of the cationic to neutral monomer units be selected to give a copolymer having a cationic charge.

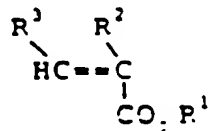
U.S. Patent No. 4,552,755 to Randen discloses improved oil-in-water moisturizing compositions comprising an oil phase containing at least one emollient oil and an oil soluble acrylate polymer, a water phase and an emulsifying agent. The acrylate polymer is disclosed as having a solubility parameter of 6 to 10 (cal/cc)<sup>1/2</sup> in poorly hydrogen-bonding solvents. The acrylate polymer increases the substantivity of the moisturizing composition to the skin.

U.S. Patent No. 4,172,122 to Kubik et al. discloses water resistant suncreening compositions comprising a cosmetically acceptable oil base, at least one water-insoluble ultraviolet light absorbing material which is soluble in the oil base, and a water insoluble acrylate polymer having a solubility parameter of 6 to 10 (cal/cc)<sup>1/2</sup> in weak hydrogen bonding solvents. The inclusion of the acrylate polymer renders the light absorbent material more water resistant, so that it does not wash away on exposure to water.

Oil based cleansers, such as "Gojo"<sup>TM</sup> are very effective for cleaning grease and oil based dirt without causing undue irritation to the skin. However, these compositions must themselves be cleaned off in a separate cleaning step to remove the undesirable oily residue left on the skin.

#### Summary of the Invention

The present invention is drawn to a skin-cleansing composition comprising a soap composition, a soap/synthetic "combo" composition or a synthetic detergent composition wherein the composition comprises an effective amount of a mildness additive that is a non-water soluble acrylate polymer that is soluble in poorly hydrogen bonding solvents or solvent blends having a solubility parameter of between about 8.4 and 10.4 (cal/cc)<sup>1/2</sup>. The soap composition, soap/synthetic "combo" composition or synthetic detergent composition is a cleansing component having the effect of drying or irritating the skin when it does not contain the mildness additive. The polymer comprises monomers of the formula:



wherein  $R^1$  is H or an alkyl radical containing 1 to 18 carbon atoms in cyclic, straight- or branched-chain configuration and is saturated or unsaturated;  $R^2$  is hydrogen, lower alkyl or  $-CH_2CO_2R^1$ ; and  $R^3$  is hydrogen, methyl or  $--CO_2R^1$ ; provided, that when  $R^2$  is not hydrogen,  $R^3$  is hydrogen, and when  $R^3$  is not hydrogen,  $R^2$  is hydrogen.

The incorporation of the indicated polymers reduces the drying and irritating effect of conventional cleansing compositions on the skin.

#### Description of Presently Preferred Embodiments

The mildness additives to be incorporated into conventional skin cleansing compositions according to the present invention are acrylate polymers specifically selected to provide the appropriate solubility parameter for the cleansing composition to be used. These acrylate polymers comprise the indicated monomers selected in any manner that will provide the desired solubility parameter for the overall polymer as indicated.

A preferred method of achieving this solubility parameter is by providing certain mole ratio ranges of monomers having identifiable physical property characteristics. In this manner, a suitable mildness additive may be prepared as a polymer that comprises hydrophilic monomers, fatty monomers and soft monomers. The monomers are characterized as belonging in various classes by measuring various physical parameters of homopolymers comprised of the corresponding monomer.

Hydrophilic monomers are identified as being soluble in strongly hydrogen bonding solvents or solvent blends that have a solubility parameter of between about 9.4 and 14  $(\text{cal/cc})^{1/2}$ . These monomers preferably constitute about 5 to 40 mole percent of the mildness additive polymer, and more preferably constitute about 10 to 25 mole percent.

Specific examples of hydrophilic monomers to be used in the acrylate polymers of the mildness additives are unesterified  $\alpha, \beta$ -olefinically unsaturated carboxylic acids such as acrylic acid, methacrylic acid, maleic acid, itaconic acid and the like. When the monomers are difunctionally acidic, half the amount of this monomer would be used.

Monomers that are fatty in nature comprise acrylates or methacrylates that contain about 11 or more carbons in the alcohol portion of the monomer. These monomers preferably constitute about 10 to 60 mole percent of the mildness additive polymer, and more preferably constitute about 30 to 50 mole percent.

Specific examples of the "fatty" monomers that may be selected for use in the mildness additives of the present invention are:

- undecyl acrylate
- undecyl methacrylate
- lauryl acrylate
- lauryl methacrylate
- hexadecyl acrylate
- hexadecyl methacrylate
- octadecyl acrylate
- octadecyl methacrylate
- stearyl methacrylate

Soft monomers are defined as monomers of which the corresponding homopolymer prepared from the monomer has a glass transition temperature ( $T_g$ ) between about  $-70$  and  $20^\circ\text{C}$ . These monomers preferably constitute about 20 to 70 mole percent of the mildness additive polymer, and more preferably constitute about 30 to 50 mole percent.

Especially preferred soft monomers to be used in the acrylate polymers of the mildness additives are:

- n-propyl acrylate
- n-butyl acrylate
- n-butyl methacrylate
- iso-butyl acrylate



- iso-butyl methacrylate
- sec-butyl acrylate
- sec-butyl methacrylate
- n-amyl acrylate
- 5 n-amyl methacrylate
- iso-amyl acrylate
- iso-amyl methacrylate
- n-hexyl acrylate
- n-hexyl methacrylate
- 10 cyclohexyl acrylate
- 2-ethylbutyl acrylate
- 2-ethylbutyl methacrylate
- n-heptyl acrylate
- n-heptyl methacrylate
- 15 n-octyl acrylate
- n-octyl methacrylate
- 2-ethylhexyl acrylate
- 2-ethylhexyl methacrylate
- iso-octyl acrylate
- 20 n-nonyl acrylate
- n-nonyl methacrylate
- n-decyl acrylate
- n-decyl methacrylate
- iso-decyl acrylate
- 25 iso-decyl methacrylate

The incorporation of non-acrylate monomers, such as N-vinyl pyrrolidone, vinyl acetate or of acrylates substituted by functional groups such as amine or hydroxyl

30 functionalities is contemplated, provided that the ultimate mildness additive polymer is soluble in the solvents or solvent blends as indicated. Similarly, "hard" acrylate or methacrylate monomers (monomers wherein the  $T_g$  of the corresponding homopolymer is greater than about 20° C) may

35 also be incorporated in the mildness additive polymer in a minor amount.

The mildness additives of the present invention are incorporated into conventional cleansing compositions in an amount effective to reduce the drying and irritating effect of these compositions on the skin. Typically, the mildness additive comprises between about 0.5 and 5 percent by weight of the total composition.

The mildness additives of the present invention add a substantive component to a cleansing composition due to the physical nature of the polymer and its unique solubility parameter. While not being bound by theory, it is believed that the retention of some of the mildness additive on the skin during and after cleansing leads to simultaneous retention of natural oils and moisture in the skin, so that the skin does not dry out as much as occurs with washing with ordinary cleansing compositions.

Foaming is an important and desirable property of a successful cleansing composition, and because the mildness additives of the present invention act as a poor surfactant, they do not kill the foam provided by the balance of the skin cleansing composition. Additionally, when the skin cleansing composition is in the form of a bar, the mildness additive will reduce the cracking of the bar that would otherwise be observed in use.

The preparation of the polymers from the olefinically unsaturated monomers is well documented in the literature and can be carried out by standard bulk, solution or emulsion techniques. Generally, the latter two are preferred with solution polymerization being most preferred. The polymerization of the monomers is catalyzed by free radical-generating catalysts such as peroxides, azo catalysts and the like. To be most effective, the reactor for such polymerization should be purged with an inert gas in order to remove traces of oxygen. The solution polymerizations are run in a compatible solvent and the final polymer solution preferably contains 25 to 60 percent solids. Preferably, the polymers are prepared in a fatty acid solvent that is compatible with the ultimate skin

cleansing composition, such as Hystrene 1835 (commercially available from Witco Chemical Corp., Memphis, TN) and Emery 627 fatty acids (commercially available from Emery Industries, Inc., Cincinnati, OH).

5       The molecular weight of the acrylate polymers used in the compositions may vary over a broad range. Preferably, the weight average molecular weight of the polymer is in the range of about 50,000 to 2.5 million, and most preferably between about 200,000 and 1 million. These  
10 weight average molecular weights are measured by GPC based on calibration of polystyrene standards. Generally, these polymers will have a Brookfield viscosity between 50 and 10,000 cps., and preferably between 100 and 1,000 cps., when measured at 10 percent solids at 40°C.

15       The mildness additives useful in cleansing compositions are insoluble in water and must be soluble in poorly hydrogen-bonding solvents or solvent blends that have a solubility parameter of between about 8.4 and 10.4 (cal/cc)<sup>1/2</sup>. Preferably, the mildness additives are  
20 soluble in such solvents or solvent blends that have a solubility parameter of between about 8.9 and 9.8 (cal/cc)<sup>1/2</sup>.

      The solubility of polymers in solvents with identified solubility parameters is determined according to the method  
25 generally described in Polymer Handbook (edited by Bandrup and Immergut, 1966), pages IV- 344-358. Specifically, a small amount of solid polymer (about 1 gram) is placed in a test tube and enough of a selected solvent is added such that the final solution has about 3% solids content. The  
30 mixture is observed to determine if the polymer is soluble in the solvent. This experiment is repeated over a range of solvents having known solubility parameter values. An extensive list of solvents (classified as either poorly hydrogen-bonding, moderately hydrogen-bonding, or strongly  
35 hydrogen-bonding) are described in this handbook.

      The soap, soap/synthetic "combo" compositions or the synthetic detergent compositions to which the mildness

additives of the present invention are added are the conventional skin cleansing compositions in the art that have the effect of drying or irritating the skin. These compositions typically contain at least 15% of a surfactant by weight. Typically, these compositions contain between about 20 and 80% of surfactant by weight. Preferred liquid skin cleansing compositions comprise between about 30 and 40% surfactant by weight. Preferred bar skin cleansing compositions comprise between about 50 and 80% surfactant by weight.

Traditional soaps comprise the alkali metal salts of long-chain monocarboxylic acids having an alkyl chain length of between about  $C_8$  to  $C_{18}$ , such as sodium tallowate, sodium cocoate, sodium palmitate and the like. Synthetic detergents are cleansing compositions that contain alkali metal soaps of non-natural acids that are fatty in nature, such as sodium acyl isethionate, sodium lauryl alcohol sulfate, sodium monoalkyl sulfosuccinate, and the like. The soap/synthetic compositions are combinations of soaps and synthetic detergents.

The cleansing compositions of the present invention may additionally comprise pigments, dyes, perfumes, germicides, antioxidants or other such components as are conventional in the cleansing composition art. For example, antibacterial agents such as phenol, cresylic acid, 3,4,4'-trichloro carbanilide and 2-hydroxy-2',4,4'-trichloro diphenyl ether may be incorporated. Where desired, superfatting agents such as unsaponified oil, fatty acid, lanolin, mineral oil, fatty ester or fatty alcohols may also be present. In the case of slightly abrasive soaps, a finely powdered insoluble material such as pumice, alkaline builders such as sodium silicate, sodium carbonate, or trisodium phosphate, or microencapsulated moisturizers, such as used in Bu<sup>®</sup> Pu<sup>®</sup> Daily Cleanser, may be used. Transparent soaps containing the mildness additives of the present invention may be prepared by addition of alcohol, sugar solution and glycerol in a conventional manner. Transparent soaps, it

is noted, may also be made by controlled mixing of the soap at specified temperatures in a manner conventional in the art.

The appropriate relative ratios of monomer groups, and consequently the desired solubility parameter of the resulting polymer, are best selected by use of design experiment methods. Thus, a selection of polymers having the indicated solubility parameter is prepared using two or more monomers, with variation of the mole percentage content of the monomers. These mildness additives are incorporated into the selected cleansing compositions, and a test is performed to compare the effect of repeated washing on the skin of hands. One such test is the modified Highley Test described in the Evaluation of Efficacy section below. Additional polymers are prepared that are more closely related to the additive that has the least detrimental or most beneficial effect on skin in the first design experiment. A second series of tests are performed on this second group of compositions to "fine-tune" the selection of monomer content of the mildness additive.

The following examples are illustrative in nature only, and are not intended to limit the scope of the invention.

#### PREPARATION OF MILDNESS ADDITIVE

The acrylate polymers were prepared in ethyl acetate and were solvent exchanged at reduced pressures with  $C_{18}$  fatty acids (Hystrene 1835, commercially available from Witco Chemical Corp., Memphis, TN), to provide a polymer in Hystrene 1835 content of 10% solids. These mixtures were added to about one third the amount by weight of a 1:1 ratio Tallow/coco fatty acid blend for incorporation into the bars. Some of the polymers prepared and evaluated are shown in Table I.

PREPARATION OF TRANSPARENT COMBO-BAR

<u>Solution A:</u>		<u>% by wt.</u>
1.	Triethanolamine, 99%	27.5
5 2.	sorbitol, 70%	3.93
3.	glycerine, 99%	3.53
4.	"Surfine AZI-A"	2.50
5.	"Finsolve TN"	2.00
6.	"Tauranol I-78"	10.00

10

"Surfine AZI-A", "Finsolve TN" and "Tauranol I-78" are all commercially available from Finetex Inc., Elmwood Park, NJ.

15 Liquids 1-5 were combined and heated with stirring under N<sub>2</sub> to 70°C ± 5°C. Tauranol (6) was added, and the temperature of the composition was maintained until it dissolved.

<u>Solution B:</u>		<u>% by wt.</u>
20 7.	10% polymer in Hystrene 1835	26.55
8.	Tallow/coco fatty acid blend (1:1 ratio)	8.50

25 Components 7 and 8 were combined and heated to 60°C ± 2°C until they dissolved.

<u>Solution C:</u>		<u>% by wt.</u>
9.	NaOH	4.04
10.	NaCl	0.21
30 11.	Water	11.24

Components 9 and 10 were combined in 11.

35 Solution B (at 60°C ± 2°C) and solution C were added simultaneously to solution A at 70°C ± 5°C with good stirring and N<sub>2</sub> purge for 10 minutes. The mixer and N<sub>2</sub> gas were turned off and the bubbles were allowed to rise. The

foam was skimmed off and the liquid was poured into bar soap molds.

### Evaluation of Efficacy

5 The mildness of the bar soaps was evaluated via a modified Highley induced dryness test which measures the effectiveness of a product to prevent the formation of dry, chapped hands. In this test, participants wash the backs of one of their hands with a test bar and the other with a control bar not containing the polymer. The hands are air dried after each washing. This is repeated for a total of 10 5 washings each day for four days. One hour after the last washing each day the hands are scored on a scale of 0-5 with respect to dry, scaly chapped hands. A 0 rating is best and a 5 rating worst. The Highley values appear in 15 Table I, which are normalized with the control so that a bar with no additive would receive a Highley score of 0 and higher numbers indicate better prevention of dry, chapped hands.

20

TABLE I

#### Polymer Composition and Highley Scores

##### A. First Design

<u>Polymer Mole Percent</u>				
	<u>Acrylic</u>	<u>Stearyl</u>	<u>Iso-octyl</u>	<u>Highley</u>
25	<u>Acid</u>	<u>Methacrylate</u>	<u>Acrylate</u>	<u>Score</u>
	1. 15	20	65	1.17
	2. 35	20	45	0.48
	3. 15	40	45	2.66
	4. 35	40	25	0.75
30	5. 25	30	45	0.52
	6. 25	30	45	0.28

##### B. Second Design

35	7. 10	35	55	0.56
	8. 20	35	45	0.21
	9. 10	45	45	0.29

10.	20	45	35.	1.02
11.	15	40	45	0.44
12.	15	40	45	0.75

5 Note: The Highley scores of the First and Second Design cannot be compared to each other. The First Design experiment was conducted with no pretreatment of the hands. In the Second Design experiment, the subjects were first required to wash their hands with a harsh soap, so the  
10 Highley score actually represents an improvement over initially dry skin.

A score of 2.66 for No. 3 polymer represents a very, very significant improvement over the control bar for the prevention of dry skin. The second design experiment shows  
15 that No. 10 polymer is an even better mildness additive for this particular cleansing formulation.

20

25

30

35

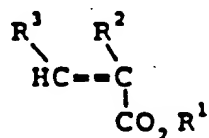


CLAIMS:

1. A skin-cleansing composition consisting essentially of

5 a) a cleansing component selected from a soap composition, a soap/synthetic "combo" composition or a synthetic detergent composition, said cleansing component characterized by having the effect of drying or irritating skin, and

10 b) a non-water soluble acrylate polymer that is soluble in poorly hydrogen bonding solvents or solvent blends that have a solubility parameter of between about 8.4 and 10.4 (cal/cc)<sup>1/2</sup> in an amount effective to reduce the drying or irritating effect of component a) on the  
15 skin, said polymer comprising monomers of the formula:



20 wherein R<sup>1</sup> is H or an alkyl radical containing 1 to 18 carbon atoms in cyclic, straight- or branched-chain configuration and is saturated or unsaturated; R<sup>2</sup> is hydrogen, lower alkyl or -CH<sup>2</sup>CO<sub>2</sub>R<sup>1</sup>; and R<sup>3</sup> is hydrogen,  
25 methyl or -CO<sub>2</sub>R<sup>1</sup>; provided, that when R<sup>2</sup> is not hydrogen, R<sup>3</sup> is hydrogen, and when R<sup>3</sup> is not hydrogen, R<sup>2</sup> is hydrogen.

30 2. The composition of claim 1, wherein said polymer comprises

- a) ~~about~~ 5 to 40 mole percent of an monomer of which the corresponding homopolymer is hydrophilic;
- b) ~~about~~ 10 to 60 mole percent of an monomer of which the corresponding homopolymer is fatty  
35 in nature; and
- c) ~~about~~ 20 to 70 mole percent of an monomer of which the corresponding homopolymer is soft in nature.

3. The composition of claim 2, wherein said polymer comprises

- 5       ~~about~~ 10-25 mole percent of monomer a);  
      ~~about~~ 30-50 mole percent of monomer b); and  
      ~~about~~ 30-50 mole percent of monomer c).

4. The composition of claim 2, wherein said polymer comprises

- 10       a) ~~about~~ 5 to 40 mole percent of a hydrophilic monomer selected from the group consisting of acrylic acid, methacrylic acid, maleic acid and itaconic acid;
- 15       b) ~~about~~ 10 to 60 mole percent of a fatty monomer selected from the group consisting of undecyl acrylate, undecyl methacrylate, lauryl acrylate, lauryl methacrylate, hexadecyl acrylate, hexadecyl methacrylate, octadecyl acrylate, octadecyl methacrylate and stearyl methacrylate; and
- 20       c) ~~about~~ 20 to 70 mole percent of a soft monomer selected from the group consisting of n-propyl acrylate, n-butyl acrylate, n-butyl methacrylate, iso-butyl acrylate, iso-butyl methacrylate, sec-butyl acrylate, sec-butyl
- 25       methacrylate, n-amyl acrylate, n-amyl methacrylate, iso-amyl acrylate, iso-amyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, cyclohexyl acrylate, 2-ethylbutyl acrylate, 2-ethylbutyl
- 30       methacrylate, n-heptyl acrylate, n-heptyl methacrylate, n-octyl acrylate, n-octyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, iso-octyl acrylate, n-nonyl acrylate, n-nonyl
- 35       methacrylate, n-decyl acrylate, n-decyl methacrylate, iso-decyl acrylate and iso-decyl methacrylate.

5. The composition of claim 4, wherein said polymer comprises

5 a) ~~about~~ 10 to 25 mole percent of a hydrophilic monomer selected from the group consisting of acrylic acid, methacrylic acid, maleic acid and itaconic acid;

10 b) ~~about~~ 30 to 50 mole percent of a fatty monomer selected from the group consisting of undecyl acrylate, undecyl methacrylate, lauryl acrylate, lauryl methacrylate, hexadecyl acrylate, hexadecyl methacrylate, octadecyl acrylate, octadecyl methacrylate and stearyl methacrylate; and

15 c) ~~about~~ 30 to 50 mole percent of a soft monomer selected from the group consisting of n-propyl acrylate, n-butyl acrylate, n-butyl methacrylate, iso-butyl acrylate, iso-butyl methacrylate, sec-butyl acrylate, sec-butyl methacrylate, n-amyl acrylate, n-amyl methacrylate, iso-amyl acrylate, iso-amyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, cyclohexyl acrylate, 2-ethylbutyl acrylate, 2-ethylbutyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, n-octyl acrylate, n-octyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate, iso-octyl acrylate, n-nonyl acrylate, n-nonyl methacrylate, n-decyl acrylate, n-decyl methacrylate, iso-decyl acrylate and iso-decyl methacrylate.

6. The composition of claim 5, wherein said polymer comprises

35 a) ~~about~~ 10 to 25 mole percent of a hydrophilic monomer selected from the group consisting of acrylic acid and methacrylic acid;

- b) ~~about~~ 30 to 50 mole percent of a fatty monomer that is stearyl methacrylate; and
- c) ~~about~~ 30 to 50 mole percent of a soft monomer selected from the group consisting of n-butyl acrylate, n-butyl methacrylate, iso-butyl acrylate, iso-butyl methacrylate, sec-butyl acrylate, sec-butyl methacrylate, n-amyl acrylate, n-amyl methacrylate, iso-amyl acrylate, iso-amyl methacrylate, n-hexyl acrylate, n-hexyl methacrylate, cyclohexyl acrylate, 2-ethylbutyl acrylate, 2-ethylbutyl methacrylate, n-heptyl acrylate, n-heptyl methacrylate, n-octyl acrylate, n-octyl methacrylate, 2-ethylhexyl acrylate, 2-ethylhexyl methacrylate and iso-octyl acrylate.

7. The composition of claim 1, wherein said polymer comprises between ~~about~~ 0.5 and 5 percent by weight of the total composition.

8. The composition of claim 1 comprising an alkali metal soap of a fatty acid having an alkyl chain length of between about  $C_4$  to  $C_{22}$ .

9. The composition of claim 1 further comprising glycerine.

10. The composition of claim 1, wherein said composition is in the form of a bar.

11. The composition of claim 1, wherein said composition is in the form of a liquid.

12. The composition of claim 1, wherein said polymer is soluble in poorly hydrogen bonding solvents or solvent blends that have a solubility parameter of between ~~about~~ 8.9 and 9.8 (cal/cc)<sup>1/2</sup>.

13. The composition of claim 1, wherein said  
cleansing component comprises at least 15% surfactant.

14. The composition of claim 1, wherein said  
5 cleansing component comprises between 20 and 80%  
surfactant.

15. The composition of claim 10, wherein said  
cleansing component comprises between ~~about~~ 50 and 80% by  
10 weight surfactant.

16. The composition of claim 11, wherein said  
cleansing component comprises between ~~about~~ 30 and 40% by  
weight surfactant.

15

20

25

30

35



## INTERNATIONAL SEARCH REPORT

International Application No

PCT/US 91/02443

## I. CLASSIFICATION OF SUBJECT MATTER (If several classification symbols apply, indicate all)\*

According to International Patent Classification (IPC) or to both National Classification and IPC  
 Int.C1.5 A 61 K 7/48 C 11 D 3/37

## II. FIELDS SEARCHED

Minimum Documentation Searched<sup>7</sup>

Classification System	Classification Symbols
Int.C1.5	A 61 K C 11 D

Documentation Searched other than Minimum Documentation  
 to the Extent that such Documents are Included in the Fields Searched<sup>8</sup>

III. DOCUMENTS CONSIDERED TO BE RELEVANT<sup>9</sup>

Category *	Citation of Document, <sup>11</sup> with indication, where appropriate, of the relevant passages <sup>12</sup>	Relevant to Claim No. <sup>13</sup>
Y	US-A-4 552 755 (RANDEN) 12 November 1985, see column 2, line 5 - column 6, line 9; examples 5-18; claims 1 and 3 (cited in the application) ---	1-8, 11
Y	GB-A-2 144 133 (L'OREAL) 27 February 1985, see page 1, line 1 - page 3, line 12; claims ---	1-8, 11
A	FR-A-2 398 496 (MINNESOTA MINING AND MANUFACTURING CO.) 23 February 1979, see example 1; claims & US-A-4 172 122 (cited in the application) -----	1-5, 11

Y	US-A-4 552 755 (RANDEN) 12 November 1985, see column 2, line 5 - column 6, line 9; examples 5-18; claims 1 and 3 (cited in the application) ---	1-8, 11
Y	GB-A-2 144 133 (L'OREAL) 27 February 1985, see page 1, line 1 - page 3, line 12; claims ---	1-8, 11
A	FR-A-2 398 496 (MINNESOTA MINING AND MANUFACTURING CO.) 23 February 1979, see example 1; claims & US-A-4 172 122 (cited in the application) -----	1-5, 11

\* Special categories of cited documents: <sup>10</sup>

"A" document defining the general state of the art which is not considered to be of particular relevance

"E" earlier document but published on or after the international filing date

"L" document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)

"O" document referring to an oral disclosure, use, exhibition or other means

"T" document published prior to the international filing date but later than the priority date claimed

"T" later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention

"X" document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step

"Y" document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art.

"A" document member of the same patent family

## IV. CERTIFICATION

Date of the Actual Completion of the International Search

31-07-1991

Date of Mailing of this International Search Report

17.09.91

International Searching Authority

EUROPEAN PATENT OFFICE

Signature of Authorized Member

D. Haer

# ANNEX TO THE INTERNATIONAL SEARCH REPORT ON INTERNATIONAL PATENT APPLICATION NO.

US 9102443

SA 46965

This annex lists the patent family members relating to the patent documents cited in the above-mentioned international search report. The members are as contained in the European Patent Office EDP file on 10/09/91. The European Patent Office is in no way liable for these particulars which are merely given for the purpose of information.

Patent document cited in search report	Publication date	Patent family member(s)	Publication date
US-A- 4552755	12-11-85	None	
GB-A- 2144133	27-02-85	FR-A- 2549842	01-02-85
		BE-A- 900210	24-01-85
		CA-A- 1218017	17-02-87
		CH-A- 659387	30-01-87
		DE-A- 3427254	07-02-85
		JP-A- 60042319	06-03-85
		US-A- 4673571	16-06-87
FR-A- 2398496	23-02-79	US-A- 4172122	23-10-79
		CA-A- 1110172	06-10-81
		DE-A, C 2833711	15-02-79
		GB-A, B 2002632	28-02-79
		JP-C- 1371682	07-04-87
		JP-A- 54041337	02-04-79
		JP-B- 61039923	06-09-86

**THIS PAGE BLANK (USPTO)**